DERWENT-ACC-NO: <u>2005-299172</u>

DERWENT-WEEK: 200531

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TITLE: Exhaust-gas purification system of engine, has carbon-dioxide absorber, catalyst which generates hydrogen by shift reaction of water vapor and carbon monoxide, and nitrogen-oxide catalyst, which are arranged in engine exhaust path

PATENT-ASSIGNEE: NISSAN MOTOR CO LTD[NSMO]

PRIORITY-DATA: 2003JP-0327394 (September 19, 2003)

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APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2005090426A	N/A	2003JP-0327394	September 19, 2003

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ABSTRACTED-PUB-NO: JP2005090426A

BASIC-ABSTRACT:

NOVELTY - A <u>carbon-dioxide absorber,</u> a hydrogen generation catalyst which generates hydrogen by shift reaction of water vapor and carbon monoxide, and a

nitrogen-oxide (NOX) catalyst are arranged in **engine** exhaust path. A measurement unit measures temperature of the absorber and the catalysts. The (NOX) catalyst adsorbs NOX from **exhaust gas,** during lean state, and reduces NOX during rich state.

DETAILED DESCRIPTION - A reducing-agent supply unit intermittently increases the reducing-agent concentration in the **exhaust gas**. A temperature increasing unit is provided to increase the **exhaust-gas** temperature. The **carbon-dioxide absorber** is arranged at the upstream side of the hydrogen generation catalyst. The hydrogen generation catalyst is arranged such that its temperature becomes 30 deg. C or more than that of the nitrogen-oxide catalyst. The **engine** speed is increased after a fixed-distance travel of the motor vehicle in which the **engine** is arranged, to increase the **exhaust-gas** temperature. The **carbon-dioxide absorber discharges carbon dioxide when engine** temperature is increased. The **engine** temperature is increased by 50 deg. C or more than the temperature at which **carbon dioxide is discharged by the absorber**. Temperature of the absorber and the NOX catalyst is set to 700-800 deg. C and 600-750 deg. C, respectively. The **absorber discharges carbon dioxide** at 700 deg. C or more. The free energy of formation of the reaction of the oxide of alkali metal and/or alkaline earth metal in the nitrogen-oxide catalyst, at 300 deg. C is smaller than that of the oxide of alkali metal and/or alkaline earth metal in the hydrogen generation catalyst. The ratio of the amount of oxide, nitrate, or carbonate present in the NOX catalyst with that in the **carbon-dioxide absorber,** is 1:4 or more.

USE - For purifying **exhaust gas** of internal combustion **engine** of motor vehicle.

ADVANTAGE - Enables generating hydrogen also in a low-temperature area by arranging the hydrogen generation catalyst near the **carbon-dioxide absorber**. Enables simultaneously regenerating the nitrogen-oxide catalyst during the discharge of the **carbon dioxide from the carbon-dioxide absorber**. Reduces the usage amount of noble metals in the system.

DESCRIPTION OF DRAWING(S) - The figure shows a schematic view of the **exhaust-gas** purification system. (Drawing includes non-English language text).

CHOSEN-DRAWING:	Dwg.1/4
TITLE-TERMS:	EXHAUST GAS PURIFICATION SYSTEM ENGINE CARBON ABSORB CATALYST GENERATE HYDROGEN SHIFT REACT WATER VAPOUR CARBON NITROGEN OXIDE CATALYST ARRANGE ENGINE EXHAUST PATH

DERWENT-CLASS: E36 H06 J01 J04 Q51 X22

CPI-CODES: E11-D; E11-E; E11-Q02A; E31-A02C; E31-H01; E31-N05C; E31-P02B; E33; E33-A04; E34; E34-D03C; E34-D03D; E34-E; E35-L; H06-C03B; J01-E02D; J04-E09A; N01-A; N01-B; N02-E02; N02-F; N03-B02; N06-A; N06-B01; N07-B; N07-C; N07-L01C1; N07-L02C; N07-L02D;

EPI-CODES: X22-A03B; X22-A03H; X22-A05F1; X22-A07;

CHEMICAL-CODES: Chemical Indexing M3 *01* Fragmentation Code C101 C550 C810 M411 M424 M720 M740 M904 M905 N105 N209 N262 N441 N513 N514 N515 Q431 Q436 Q439 Specfic Compounds 01532K 01532P Registry Numbers 1532P 1532U

Chemical Indexing M3 *02* Fragmentation Code C107 C108 C520 C730 C800 C801 C802 C803 C804 C807 M411 M424 M740 M750 M904 M905 N105 N163 Q431 Q436 Q439 Specfic Compounds 01901K 01901X Registry Numbers 1901U

Chemical Indexing M3 *03* Fragmentation Code C108 C307 C520 C730 C800 C801 C802 C803 C804 C807 M411 M424 M740 M750 M904 M905 M910 N105 N163 Q431 Q436 Q439 Specfic Compounds 01902K 01902X Registry Numbers 1902U

Chemical Indexing M3 *04* Fragmentation Code C107 C108 C307 C520 C730 C800 C801 C802 C803 C804 C807 M411 M424 M740 M750 M904 M905 M910 N105 N163 Q431 Q436 Q439 Specfic Compounds 01881K 01881X Registry Numbers 1881U

Chemical Indexing M3 *05* Fragmentation Code C101 C108 C550 C730 C800 C801 C802 C804 C805 C807 M411 M730 M904 M905 M910 Specfic Compounds 01740K 01740S Registry Numbers 1740S 1740U

Chemical Indexing M3 *06* Fragmentation Code C106 C108 C550 C730 C800 C801 C802 C803 C805 C807 M411 M730 M904 M905 M910 Specfic Compounds 01423K 01423S Registry Numbers 1423S 1423U

Chemical Indexing M3 *07* Fragmentation Code C106 C108 C530 C730 C800 C801 C802 C803 C805 C807 M411 M424 M720 M740 M750 M904 M905 M910 N105 N163 N202 N209 N242 N262 N309 N343 N441 N513 N514 N515 Q431 Q436 Q439 Specfic Compounds

01066K 01066P 01066X Registry Numbers 1066P 1066U

Chemical Indexing M3 *08* Fragmentation Code A758 A940 C108
C550 C730 C801 C802 C803 C804 C805 C807 M411 M424 M730
M740 M782 M904 M905 M910 N105 N163 Q421 Q431 Q436 Q439
Q508 R032 R036 Specfic Compounds 01506K 01506C 01506M
01506R Registry Numbers 1506S 1506U

Chemical Indexing M3 *09* Fragmentation Code A100 A111 A200
A313 A940 B114 B701 B712 B720 B831 C108 C802 C803 C804
C805 C807 M411 M417 M423 M424 M730 M740 M782 M904 M905
N105 N163 Q421 Q431 Q436 Q439 Q508 R044 Specfic Compounds
07707K 07707C 07707M 07707R A05LVK A05LVC A05LVM
A05LVR

Chemical Indexing M3 *10* Fragmentation Code A678 C810 M411
M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436
Q439 Q508 R036 Specfic Compounds 03247K 03247C 03247M
03247R

Chemical Indexing M3 *11* Fragmentation Code A545 C810 M411
M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436
Q439 Q508 R036 Specfic Compounds 06899K 06899C 06899M
06899R

Chemical Indexing M3 *12* Fragmentation Code A103 A540 A940
C108 C550 C730 C801 C802 C803 C804 C805 C807 M411 M424
M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439
Q508 R032 R036 Specfic Compounds A40NSK A40NSC A40NSM
A40NSR

Chemical Indexing M3 *13* Fragmentation Code A111 A940 C108
C550 C730 C801 C802 C803 C804 C805 C807 M411 M424 M730
M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439 Q508
R032 R036 Specfic Compounds 01517K 01517C 01517M 01517R
A28AGK A28AGC A28AGM A28AGR Registry Numbers 1517S
1517U

Chemical Indexing M3 *14* Fragmentation Code A238 A940 C108
C550 C730 C801 C802 C803 C804 C805 C807 M411 M424 M730
M740 M782 M904 M905 M910 N105 N163 Q421 Q431 Q436 Q439
Q508 R032 R036 Specfic Compounds 01519K 01519C 01519M

01519R Registry Numbers 1519S 1519U

Chemical Indexing M3 *15* Fragmentation Code A212 A313 A426 A940 B114 B701 B712 B720 B831 C108 C802 C803 C804 C805 C807 M411 M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439 Q508 R044 Specfic Compounds 07142K 07142C 07142M 07142R 09127K 09127C 09127M 09127R

Chemical Indexing M3 *16* Fragmentation Code A256 A940 C108 C550 C730 C800 C801 C802 C803 C804 C805 C807 M411 M424 M730 M740 M782 M904 M905 M910 N105 N163 Q421 Q431 Q436 Q439 Q508 R032 R036 Specfic Compounds 01499K 01499C 01499M 01499R Registry Numbers 1499S 1499U

Chemical Indexing M3 *17* Fragmentation Code A100 A200 A940 C106 C108 C307 C510 C730 C801 C802 C803 C804 C805 C807 M411 M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439 Q508 R032 R036 Markush Compounds 200154-36401-K 200154-36401-C 200154-36401-M 200154-36401-R

Chemical Indexing M3 *18* Fragmentation Code A100 A200 A540 A940 C108 C550 C730 C801 C802 C803 C804 C805 C807 M411 M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439 Q508 R032 R036 Markush Compounds 200154-36402-K 200154-36402-C 200154-36402-M 200154-36402-R

Chemical Indexing M3 *19* Fragmentation Code A100 A200 A540 A940 C106 C108 C730 C801 C802 C803 C805 C807 M411 M424 M730 M740 M782 M904 M905 N105 N163 Q421 Q431 Q436 Q439 Q508 R032 R036 Markush Compounds 200154-36403-K 200154-36403-C 200154-36403-M 200154-36403-R

UNLINKED-DERWENT- ; 1066P ; 1066U ; 1423S ; 1423U ; 1499S ; 1499U ; 1506S ;
REGISTRY-NUMBERS: 1506U ; 1517S ; 1517U ; 1519S ; 1519U ; 1532P ; 1532U ;
1740S ; 1740U ; 1881U ; 1901U ; 1902U

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C2005-092816

Non-CPI Secondary Accession Numbers: N2005-245483

CLAIMS

[Claim(s)]
[Claim 1]
It has a means to measure the temperature of the internal combustion engine which operates under a hyperoxia ambient atmosphere, CO_2 absorber, H_2 generation catalyst and the NOx catalyst arranged in this internal combustion engine's exhaust gas passage, these CO_2 absorber and H_2 generation catalyst, and an NOx catalyst, the reduction component increase means which can increase the reduction constituent concentration in exhaust gas intermittently, and the means which raises exhaust gas temperature,
It is the exhaust gas purification system characterized by for the above-mentioned H_2 generation catalyst generating hydrogen by the gas water gas shift reaction from a steam and a carbon monoxide, and for the above-mentioned NOx catalyst adsorbing NOx in the exhaust gas discharged by this internal combustion engine at the time of Lean, and carrying out reduction purification at the time of rich.
[Claim 2]
The exhaust gas purification system according to claim 1 characterized by arranging the above-mentioned H_2 generation catalyst so that it may become temperature higher 30 degrees C or more than the above-mentioned NOx catalyst, arranging the CO_2 above-mentioned absorber in the upstream from the same part as the above-mentioned H_2 generation catalyst, or this H_2 generation catalyst, and changing.
[Claim 3]
The exhaust gas purification system according to claim 1 or 2 characterized by arranging the CO_2 above-mentioned absorber in the same part as this H_2 generation catalyst, and making the upstream into high concentration.
[Claim 4]
An exhaust gas purification system given in any one term of claims 1-3 characterized by raising an engine speed after fixed distance transit as a means which the above-mentioned internal combustion engine is car motor, and raises the above-mentioned exhaust gas temperature.
[Claim 5]
An exhaust gas purification system given in any one term of claims 1-4 to which the exhaust gas by which the temperature up was carried out with the means which raises the above-mentioned exhaust gas temperature is characterized by making CO_2 emit from the CO_2 above-mentioned absorber.
[Claim 6]
An exhaust gas purification system given in any one term of claims 1-5 characterized by being under temperature with the exhaust gas higher 50 degrees C than beyond the temperature to which CO_2 absorber emits CO_2, and its temperature by which the temperature up was carried out with the means which raises the above-mentioned exhaust gas temperature.
[Claim 7]
An exhaust gas purification system given in any one term of claims 1-6 characterized by making temperature of the CO_2 above-mentioned absorber into 700 degrees C or more less than 800 degrees C,

and making temperature of an NOx catalyst into 600 degrees C or more less than 750 degrees C.
[Claim 8]
An exhaust gas purification system given in any one term of claims 1-7 characterized by using what emits CO_2 above 700 degrees C as the CO_2 above-mentioned absorber.
[Claim 9]
An exhaust gas purification system given in any one term of claims 1-8 to which the above-mentioned H2 generation catalyst is characterized by being the oxide, carbonate, or nitrate containing at least one sort of elements chosen from the group to which the CO_2 above-mentioned absorber changes from alkali metal and alkaline earth metal including platinum and a cerium oxide.
[Claim 10]
The exhaust gas purification system according to claim 9 characterized by for the above-mentioned alkali oxide being a multiple oxide with a zirconium, and the above-mentioned alkali carbonate being a compound carbonate with a zirconium.
[Claim 11]
The exhaust gas purification system according to claim 9 or 10 by which the CO_2 above-mentioned absorber is characterized by including platinum further.
[Claim 12]
An exhaust gas purification system given in any one term of claims 1-11 to which the CO_2 above-mentioned absorber is characterized by containing 200g or more per catalyst
[Claim 13]
The above-mentioned NOx catalyst changes including the oxide, carbonate, or nitrate containing at least one sort of elements chosen from the group which consists of platinum and/or a rhodium, a cerium oxide, and alkali metal and alkaline earth metal,
An exhaust gas purification system given in any one term of claims 1-12 characterized by free-energy-of-formation deltaG of the reaction of the oxide of the this alkali metal and/or alkaline earth metal in 300 degrees C and CO_2 being smaller than the deltaG concerned of the oxide of the alkali metal contained in H2 generation catalyst, and/or alkaline earth metal.
[Claim 14]
The exhaust gas purification system according to claim 13 characterized by the ratio of the amount of at least one sort of oxides, carbonate or nitrate chosen from the group which consists of the alkali metal and alkaline earth metal which are contained in the above-mentioned NOx catalyst, and CO_2 absorber being 1:4 or more.
[Claim 15]
An exhaust gas purification system given in any one term of claims 1-14 by which it is characterized [which are characterized by the above-mentioned NOx catalyst containing a zeolite].
[Claim 16]
An exhaust gas purification system given in any one term of claims 1-15 to which the CO_2 above-mentioned absorber is characterized by an NOx catalyst containing barium including a lithium.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[Field of the Invention]
[0001]
This invention relates to an exhaust gas purification system, and relates to the exhaust gas purification system which reproduces the NOx catalyst which adsorbed and purified NOx contained in the exhaust gas of the internal combustion engine which operates under a hyperoxia ambient atmosphere (under lean atmosphere) in the low-temperature region (200-250 degrees C), and was further made into the detail S poisoning by the pyrosphere (600-650 degrees C).
[Background of the Invention]
[0002]
NOx is adsorbed in the Lean region and the catalyst which is made to emit NOx at the time of SUTOIKI - rich, and is purified is known so that it may be represented by the catalyst which various catalysts which purify NOx of the Lean region from the former are proposed, for example, supported platinum (Pt) and a lanthanum (La) to porosity support (for example, patent reference 1 reference).
[Patent reference 1] JP,5-168860,A
[Description of the Invention]
[Problem(s) to be Solved by the Invention]
[0003]
By the lean burn engine or the diesel power plant, NOx has so far been purified using an NOx adsorption catalyst. This NOx adsorption catalyst is the following I - Ha.
b. The function to adsorb NOx
b. The function desorbed from NOx to which it stuck
c. The function which purifies NOx from which it was desorbed
NOx is purified using ******. Desorption and purification of NOx might not take place among these functions in a low-temperature region (250 degrees C or less).
As an approach of fully ****ing and on the other hand, purifying NOx in such a low-temperature region, use of hydrogen is effective. CO which exists in exhaust gas is specifically used, and hydrogen can be generated using a reaction called CO+H2 O->H2+CO2.
However, in recent years, since engine combustion efficiency increased for low-fuel-consumption-izing, low emission temperature-ization progressed and CO2 was contained in large quantities in exhaust gas, there was a trouble that a reaction could not progress easily.
[0004]
The place which this invention is made in view of the technical problem which such a conventional technique has, and is made into the purpose is to offer the exhaust gas purification system which has the NOx decontamination capacity excellent also in the low-temperature region 250 degrees C or less.
[Means for Solving the Problem]
[0005]
this invention persons came to complete a header and this invention for the above-mentioned technical

problem being solvable by arranging CO2 absorber with H2 generation catalyst, as a result of repeating examination wholeheartedly that the above-mentioned technical problem should be solved.
[Effect of the Invention]
[0006]
According to this invention, H2 generation reaction comes to advance also in a low-temperature region by making H2 generation catalyst intermingled or arranging CO2 absorber to near.
Moreover, this CO2 absorber does not emit CO2, unless it will make it an elevated temperature, once it absorbs CO2. Therefore, although it is made an elevated temperature and CO2 is made to emit, playback of an NOx catalyst by which poisoning was carried out with the sulfur in exhaust gas at this time can also be performed to coincidence.
Furthermore, sulfur poisoning is canceled by easy and twist low temperature by using emitted CO2 for re-carbonation of the NOx adsorption component in an NOx catalyst. Thereby, thermal resistance improves and the amount of use noble metals can be reduced.
[Best Mode of Carrying Out the Invention]
[0007]
Hereafter, the exhaust gas purification system of this invention is explained to a detail. In addition, in this specification,"%", unless it mentions specially, mass percentage is shown.
[0008]
The exhaust-gas purification system of this invention is equipped with a means measure the temperature of the internal combustion engine which operates under a hyperoxia ambient atmosphere, CO2 absorber, H2 generation catalyst and the NOx catalyst arranged in this internal combustion engine's exhaust gas passage, these CO2 absorber and H2 generation catalyst, and an NOx catalyst, the reduction component increase means which can increase the reduction constituent concentration in exhaust gas intermittently, and the means which raises exhaust gas temperature, and changes.
Thus, by arranging CO2 absorber, H2 is supplied to an NOx catalyst from H2 generation catalyst, and desorption / purification reaction of NOx advances effectively also in a low-temperature region 250 degrees C or less. Moreover, an NOx catalyst is easily reproducible by CO2 from H2 and CO2 absorber from H2 generation catalyst in the case of sulfur poisoning discharge.
[0009]
Here, the above-mentioned NOx catalyst adsorbs NOx in the exhaust gas discharged by the internal combustion engine by lean atmosphere, and purifies Adsorption NOx by making it rich intermittently. In order to make it rich intermittently, it is possible to change engine operational status, to supply reduction components (H2, CO, HC, etc.) directly, etc. For this reason, the means which raises a reduction component increase means and exhaust gas temperature is arranged, and it is intermittently made rich. In addition, the method of changing engine operational status especially is desirable, and cost can be reduced, without needing excessive equipment.
Moreover, there is also a trouble of receiving sulfur poisoning (S poisoning) in the above-mentioned NOx catalyst. Since this S poisoning is poisoning temporarily, if it is made an elevated temperature, it can cancel, but if it puts to an elevated temperature not much, endurance will tend to fall.
If Ba which is a typical NOx catalyst is taken for an example, S poisoning abreaction is expressed with BaSO4+H2+HC->BaCO3+SO2. As shown also in this formula, a sulfuric acid falls out from Ba and the function as an NOx absorber carries out re-activity because carbonic acid enters. Here, if CO2 is emitted H2 generation catalyst generating hydrogen, S poisoning abreaction will progress at lower temperature.
[0010]
As the above-mentioned NOx catalyst, what changes including platinum, a rhodium or both sides, a cerium oxide, alkali metal or alkaline earth metal and the oxide containing the thing concerning the combination of such arbitration, a carbonate, or a nitrate can be used suitably, for example.
Moreover, it is suitable for this alkali metal or alkaline earth metal that free-energy-of-formation deltaG of the reaction of those oxides and COs2 in 250 degrees C is smaller than the deltaG concerned of the oxide of the alkali metal contained in H2 generation catalyst or alkaline earth metal. Since CO2 is emitted at lower temperature at this time and S poisoning discharge is also performed at low

temperature, heat-resistant ability improves.

Here, when free-energy-of-formation deltaG shows deltaG of a reaction called A2 O+CO2 ->A2CO3 when alkali metal is set to A, and alkaline earth metal is set to B, it shows deltaG of a reaction called BO+CO2 ->BCO3. By making deltaG concerning H2 generation catalyst small, CO2 becomes that it is easy to be absorbed in the direction of an NOx catalyst. In case the thing this relation of whose is the need emits CO2 from H2 generation catalyst at the time of S poisoning discharge, it is for an NOx catalyst's absorbing a thing with the sufficient one as much as possible where temperature is lower, and CO2 emitted at that temperature, and emitting S.

[0011]

Moreover, as the above-mentioned internal combustion engine, a lean burn engine, a diesel power plant, etc. are mentioned, for example. Especially when it is car motor, with the means which raises the above-mentioned exhaust gas temperature, after fixed distance transit, an engine speed can be raised and sulfur poisoning discharge can be performed. In this case, since operability is not spoiled but an emission temperature is raised effectively, it is effective. When the sulfur concentration in a gasoline is 50 ppm, about 1 time is [that what is necessary is just a time of the catalyst engine performance not exceeding a regulation value] sufficient for the timing of this sulfur poisoning discharge. [1000] As for an engine speed, it is more desirable than an engine speed in case close [of temperature up control] is not to carry out 200-800rpm extent increase. In addition, when sulfur poisoning discharge is performed frequently, there is a possibility of spoiling operability.

Furthermore, the above-mentioned internal combustion engine is usually operated under a hyperoxia ambient atmosphere (Lean region), and the exhaust gas temperature at the time of this usual operation is 200 degrees C - 250 degrees C. In this temperature region, although the adsorption reaction of NOx advances, the reaction which ****s and purifies NOx to which it stuck does not progress well.

Then, it is effective to arrange H2 generation catalyst. The above-mentioned H2 generation catalyst generates H2 by the gas water gas shift reaction from H2O contained in the exhaust gas at the time of rich, and CO, and can supply H2 [effective] as reduction material which purifies Adsorption NOx to an NOx catalyst.

Furthermore, since, as for the latest efficient engine, an emission temperature tends to fall, the effect of CO2 is larger still again. So, in this invention, temperature (300 degrees C or more) required for H2 generation catalyst to fully generate hydrogen falls to about 280 degrees C by using CO2 absorber together with the above-mentioned H2 generation catalyst. From this, H2 generation catalyst can arrange 280 degrees C or more and an NOx catalyst so that it may become 200 degrees C - 250 degrees C. In addition, unless it uses CO2 absorber, a gas water gas shift reaction does not progress easily by no less than about 10 - 14% of CO2 contained in exhaust gas. Moreover, reduction of CO2 amount in exhaust gas shows the data with which the amount of H2 generation increases to drawing 3 .

[0012]

As the above-mentioned H2 generation catalyst, what contains platinum (Pt) and a cerium oxide, for example is suitable. In order to generate H2, adsorption of H2O must be caused on a catalyst front face, CeO2 is effective in it, and Pt is effective in a reaction with CO.

Moreover, as the CO2 above-mentioned absorber, alkali metal or alkaline earth metal and the oxide containing the thing concerning the combination of such arbitration, a carbonate, or a nitrate can be used suitably, for example. Furthermore, it is desirable that the above-mentioned alkali oxide (oxide of this alkali metal or alkaline earth metal) and an alkali carbonate are compound carbonates with Zr. Zr functions as a stabilizer of alkali.

Furthermore, as for CO2 absorber, it is desirable that Pt is included further. Since Pt desorbs S adhering to CO2 absorber, CO2 absorptivity ability can be demonstrated over a long period of time.

Furthermore, CO2 absorber is good to contain 200g or more per catalyst again. In order to continue absorbing CO2 over a long period of time, a lot of CO2 absorbers are needed.

[0013]

Moreover, the above-mentioned H2 generation catalyst can be arranged so that it may become temperature higher 30 degrees C or more than the above-mentioned NOx catalyst. As for the CO2

above-mentioned absorber, at this time, arranging in the upstream is more desirable than the same part as H2 generation catalyst, or this H2 generation catalyst. From this, H2 generation fully takes place and, thereby, NOx purification engine performance's improves. Moreover, degradation by durability can also be controlled. For example, as shown in drawing 1 and drawing 2 , it can arrange. Moreover, the above-mentioned temperature control may control the rate of flow of changing the configuration of exhaust gas passage suitably, or exhaust gas, and the residence time, and may perform them. In addition, if priority is given to reaction effectiveness and H2 generation catalyst and an NOx catalyst are arranged in the elevated-temperature section, in order for degradation of a catalyst to advance early and to control this, a lot of noble metals must be used, and it is not desirable in respect of a resource or cost.

Furthermore, when arranging the CO2 above-mentioned absorber in the same part as this H2 generation catalyst, it is desirable that the upstream makes this CO2 absorber high concentration. From this, many COs2 are absorbed in H2 generation catalyst preceding paragraph, H2 generation ability of H2 generation catalyst of the downstream increases, and the NOx purification engine performance tends to improve.

[0014]

The means which raises the above-mentioned exhaust gas temperature may make CO2 emit from CO2 absorber with the exhaust gas which carried out the temperature up. That is, CO2 absorber and H2 generation catalyst are heated by hot exhaust gas, and S poisoning discharge temperature can be fallen by emitting CO2 to H2 generation and coincidence as elevated-temperature gas.

For example, what is necessary is just to heat at 620-650 degrees C by this invention, in order to use CO2 absorber together although it is necessary to heat to 700 degrees C for S poisoning removal only with H2 generation catalyst. As for the exhaust gas which carried out the temperature up, at this time, it is desirable that it is under temperature (less than 670-700 degrees C) higher 50 degrees C than beyond the temperature to which CO2 absorber emits CO2, and its temperature. It is because the catalyst engine performance will tend to deteriorate if an emission temperature is too high.

Moreover, in order to fully perform S desorption of the CO2 emission from CO2 absorber, or an NOx catalyst, the CO2 above-mentioned absorber is made into 700 degrees C or more less than 800 degrees C, and, as for an NOx catalyst, it is desirable to consider as 600 degrees C or more less than 750 degrees C. In addition, if exhaust gas temperature is too high, it will be easy to reduce the catalyst engine performance.

Furthermore, it is desirable to use what emits CO2 above 700 degrees C as the CO2 above-mentioned absorber. For example, Li2ZrO3 etc. is mentioned.

Control of this exhaust gas temperature can be performed by interlocking the thermometry means established on each catalyst inlet port or exhaust gas passage, and the means which raises the above-mentioned exhaust gas temperature.

[0015]

Moreover, it is suitable for the ratio of the amount of the alkali metal contained in the above-mentioned NOx catalyst or alkaline earth metal and the oxide containing the thing concerning the combination of such arbitration, a carbonate or a nitrate, and the CO2 above-mentioned absorber that it is 1:4 or more. Thus, H2 and CO2 to cancel it can be supplied. [sufficient by adjusting quantitative balance with an NOx catalyst when the alkali in an NOx catalyst etc. receives S poisoning]

Furthermore, as for the above-mentioned NOx catalyst, it is desirable that a zeolite is included. From this, HC purification engine performance tends to improve in the low-temperature regions at the time of engine starting etc. (from a room temperature to 150 degrees C).

Furthermore, a lithium (Li) can be contained as the CO2 above-mentioned absorber, and barium (Ba) can be contained as an NOx catalyst again. These [Li and Ba] may be mixed and used.

[Example]

[0016]

Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples.

[0017]

(Example 1)
- H2 generation catalyst with CO2 absorber
The alumina was thrown in in the acetic-acid Ce solution, and it stirred at the room temperature for 1 hour. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 600 degrees C for 1 hour, and Powder a was obtained (Ce support concentration of this powder a is 40% as CeO2).
2% of tetra-ammine Pt oxalate solution (pH=10.5) was sunk into Powder a. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder b was obtained (Pt support concentration of this powder b is 2.23%).
450g and alumina sol were fed to 22.5g, 900g of water was fed into the magnetic ball mill, preferential grinding of the SrO which are 427.5g and CO2 absorber about Powder b was carried out, and the catalyst slurry was obtained.
After having made the catalyst slurry adhere to the nature monolith support of a KODEE light (1.0L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst of coat layer 400 g/L was acquired (the amount of SrO2 in a catalyst is 200g/piece).
[0018]
- NOx catalyst
The acetic-acid Ce water solution and the acetic-acid Ba water solution were mixed and stirred. Subsequently, the alumina was thrown in and it stirred at the room temperature for 1 hour. Then, after drying at 120 degrees C one whole day and night, it calcinated at 600 degrees C for 1 hour, and Powder A was obtained (for Ba support concentration of Powder A, 7.3% and Ce support concentration are 20% as CeO2 as BaO).
2% of tetra-ammine Pt oxalate solution (pH=10.5) was sunk into Powder A. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder B was obtained (Pt support concentration of Powder B is 1.04%).
The alumina was thrown in in the acetic-acid Zr water solution, and it stirred at the room temperature for 1 hour. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 900 degrees C for 1 hour. Furthermore, after sinking in 6% of nitric-acid Rh water solution,
It dried at 120 degrees C one whole day and night, and calcinated at 400 degrees C for 1 hour, and Powder C was obtained (for Rh support concentration of Powder C, the support concentration of 2.4% and Zr is 3%).
After sinking 2% of tetra-ammine Pt oxalate solution (pH=10.5) into Powder A and drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder D was obtained (Pt support concentration of Powder D is 3.41%).
After sinking 2% of tetra-ammine Pt oxalate solution (pH=10.5) into cerium oxide and drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder E was obtained (Pt support concentration of Powder E is 3.2%).
92.6g and a silica sol were fed to 179.9g, 900g of water was fed into the magnetic ball mill, preferential grinding of 627.5g and the powder E was carried out for the beta zeolite, and the first catalyst slurry was obtained. Moreover, 50.5g and Oxidization Ce were fed to 47.8g and alumina sol 33.9g, 900g of water was fed into the magnetic ball mill, preferential grinding of 767.8g and the powder A was carried out for Powder B, and the second catalyst slurry was obtained. furthermore, the powder C -- 81.1g and alumina sol were fed to 58.1g, 900g of water was fed into the magnetic ball mill, preferential grinding of 272.0g and the powder D was carried out [84.8 and Oxidization Ce] for 403.9g and Powder A, and the third catalyst slurry was obtained.
After having made the first catalyst slurry adhere to the nature monolith support of a KODEE light (1.2L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst A of coat layer 172.1 g/L was acquired. After having made the second catalyst slurry adhere to this catalyst A, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst B of coat layer 167.5 g/L was acquired. After having made the third catalyst slurry adhere to this catalyst

B, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst C of coat layer 97.6 g/L was acquired.
[0019]
<The evaluation approach>
Following trial (1) - (4) was performed in order, and (3) or (4) evaluation was repeated 20 times.
(1) Durability test
The exhaust air system of an engine with a displacement of 4500 cc was equipped with the catalyst, gas oil (S= 10 ppm or less) was used, 750 degrees C and NOx catalyst inlet temperature were made into 650 degrees C, and the inlet temperature of H2 generation catalyst with CO2 absorber was operated for 50 hours.
(2) Low-temperature activity trial : room temperature -200 degree C
The exhaust air system of a diesel power plant with a displacement of 2500 cc was equipped with the catalyst, the 11 mode was run, and it asked for the rate of exhaust air purification.
(3) S poisoning, S poisoning discharge processing
After having used gas oil with an S concentration of 50 ppm, making NOx catalyst inlet temperature into 250 degrees C and performing 1hr operation, S desorption processing (gas oil S= 10 ppm or less is used, inlet temperature of 720 degrees C and an NOx catalyst is made into 650 degrees C, and the inlet temperature of H2 generation catalyst with CO2 absorber is operated for 30 minutes) was performed.
(4) Elevated-temperature activity trial : 200 degrees C - 300 degrees C
The exhaust air system of a diesel power plant with a displacement of 2500 cc was equipped with the catalyst, Lean (A/F=30) 40sec-> Rich (A/F=11) 4sec was operated, and it asked for the rate of exhaust air purification in this section.
[0020]
(Example 2)
Except having used the Pt support SrO (2% of Pt support concentration) as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0021]
(Example 3)
Except having used Li2ZrO3 as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0022]
(Example 4)
Except having used aluminum 2O3 as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0023]
(Example 5)
Except having carried out SrO in 150g/piece, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0024]
(Example 6)
Except having used Na2O as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0025]
(Example 7)
The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, an evaluation trial (3) and (4) were repeated and it carried out like the example 1 except the line having performed evaluation trial (3) and (S desorption processing) once twice (spacing of S poisoning discharge having been doubled).
[0026]
(Example 8)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made 650 degrees C and NOx catalyst inlet temperature into 600 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber (CO2 having been made not to be emitted from CO2 absorber).

[0027]

(Example 9)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made inlet temperature of 720 degrees C and an NOx catalyst into 580 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber.

[0028]

(Example 10)

The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made inlet temperature of 870 degrees C and an NOx catalyst into 650 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber.

[0029]

(Example 1 of a comparison)

Except having lost the first catalyst bed, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0030]

[Table 1]

	１１モード ＨＣ転化率 （％）	（3）の処理1 回後のＮＯx 転化率（％）	（3）の処理20 回後のＮＯx 転化率（％）
実施例1	82	85	69
実施例2	80	88	75
実施例3	81	87	78
実施例4	81	83	50
実施例5	82	83	60
実施例6	81	85	52
実施例7	82	85	60
実施例8	81	80	55
実施例9	81	80	43
実施例10	82	85	62
比較例1	47	83	67

[0031]

As shown in Table 1, as for the catalyst acquired in the examples 1-10 belonging to the invention in this application, the invert ratio of HC and NOx is compatible. It turns out that especially the catalyst of examples 1-3 is excellent in the NOx invert ratio after durability. On the other hand, the first catalyst bed is not used for the catalyst acquired in the example 1 of a comparison (since there is no zeolite layer, there is no HC adsorption function.). Therefore, the cold HC engine performance gets worse. It accumulates and it turns out that HC invert ratio is low.

Moreover, if an example 1 is compared with examples 4 and 7, when the timing of the case where alkali metal is not contained in CO2 absorber, or S poisoning discharge is behind the graph of drawing 3 , it shows that the endurance of an NOx catalyst falls.
[Brief Description of the Drawings]
[0032]
[Drawing 1] It is the schematic diagram showing an example of an exhaust gas purification system.
[Drawing 2] It is the schematic diagram showing other examples of an exhaust gas purification system.
[Drawing 3] It is the graph which shows the amount of H2 generation to CO2 concentration.
[Drawing 4] It is the graph which shows the relation between the count of S poisoning discharge, and an NOx invert ratio.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

EXAMPLE

[Example]
[0016]
Hereafter, although an example explains this invention to a detail further, this invention is not limited to these examples.
[0017]
(Example 1)
- H2 generation catalyst with CO2 absorber
The alumina was thrown in in the acetic-acid Ce solution, and it stirred at the room temperature for 1 hour. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 600 degrees C for 1 hour, and Powder a was obtained (Ce support concentration of this powder a is 40% as CeO2).
2% of tetra-ammine Pt oxalate solution (pH=10.5) was sunk into Powder a. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder b was obtained (Pt support concentration of this powder b is 2.23%).
450g and alumina sol were fed to 22.5g, 900g of water was fed into the magnetic ball mill, preferential grinding of the SrO which are 427.5g and CO2 absorber about Powder b was carried out, and the catalyst slurry was obtained.
After having made the catalyst slurry adhere to the nature monolith support of a KODEE light (1.0L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst of coat layer 400 g/L was acquired (the amount of SrO2 in a catalyst is 200g/piece).
[0018]
- NOx catalyst
The acetic-acid Ce water solution and the acetic-acid Ba water solution were mixed and stirred. Subsequently, the alumina was thrown in and it stirred at the room temperature for 1 hour. Then, after drying at 120 degrees C one whole day and night, it calcinated at 600 degrees C for 1 hour, and Powder A was obtained (for Ba support concentration of Powder A, 7.3% and Ce support concentration are 20% as CeO2 as BaO).
2% of tetra-ammine Pt oxalate solution (pH=10.5) was sunk into Powder A. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder B was obtained (Pt support concentration of Powder B is 1.04%).
The alumina was thrown in in the acetic-acid Zr water solution, and it stirred at the room temperature for 1 hour. Subsequently, after drying at 120 degrees C one whole day and night, it calcinated at 900 degrees C for 1 hour. Furthermore, after sinking in 6% of nitric-acid Rh water solution,
It dried at 120 degrees C one whole day and night, and calcinated at 400 degrees C for 1 hour, and Powder C was obtained (for Rh support concentration of Powder C, the support concentration of 2.4% and Zr is 3%).
After sinking 2% of tetra-ammine Pt oxalate solution (pH=10.5) into Powder A and drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder D was

obtained (Pt support concentration of Powder D is 3.41%).

After sinking 2% of tetra-ammine Pt oxalate solution (pH=10.5) into cerium oxide and drying at 120 degrees C one whole day and night, it calcinated at 400 degrees C for 1 hour, and Powder E was obtained (Pt support concentration of Powder E is 3.2%).

92.6g and a silica sol were fed to 179.9g, 900g of water was fed into the magnetic ball mill, preferential grinding of 627.5g and the powder E was carried out for the beta zeolite, and the first catalyst slurry was obtained. Moreover, 50.5g and Oxidization Ce were fed to 47.8g and alumina sol 33.9g, 900g of water was fed into the magnetic ball mill, preferential grinding of 767.8g and the powder A was carried out for Powder B, and the second catalyst slurry was obtained. furthermore, the powder C -- 81.1g and alumina sol were fed to 58.1g, 900g of water was fed into the magnetic ball mill, preferential grinding of 272.0g and the powder D was carried out [84.8 and Oxidization Ce] for 403.9g and Powder A, and the third catalyst slurry was obtained.

After having made the first catalyst slurry adhere to the nature monolith support of a KODEE light (1.2L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst A of coat layer 172.1 g/L was acquired. After having made the second catalyst slurry adhere to this catalyst A, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst B of coat layer 167.5 g/L was acquired. After having made the third catalyst slurry adhere to this catalyst B, removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and the catalyst C of coat layer 97.6 g/L was acquired.

[0019]

<The evaluation approach>

Following trial (1) - (4) was performed in order, and (3) or (4) evaluation was repeated 20 times.

(1) Durability test

The exhaust air system of an engine with a displacement of 4500 cc was equipped with the catalyst, gas oil (S= 10 ppm or less) was used, 750 degrees C and NOx catalyst inlet temperature were made into 650 degrees C, and the inlet temperature of H2 generation catalyst with CO2 absorber was operated for 50 hours.

(2) Low-temperature activity trial : room temperature -200 degree C

The exhaust air system of a diesel power plant with a displacement of 2500 cc was equipped with the catalyst, the 11 mode was run, and it asked for the rate of exhaust air purification.

(3) S poisoning, S poisoning discharge processing

After having used gas oil with an S concentration of 50 ppm, making NOx catalyst inlet temperature into 250 degrees C and performing 1hr operation, S desorption processing (gas oil S= 10 ppm or less is used, inlet temperature of 720 degrees C and an NOx catalyst is made into 650 degrees C, and the inlet temperature of H2 generation catalyst with CO2 absorber is operated for 30 minutes) was performed.

(4) Elevated-temperature activity trial : 200 degrees C - 300 degrees C

The exhaust air system of a diesel power plant with a displacement of 2500 cc was equipped with the catalyst, Lean (A/F=30) 40sec-> Rich (A/F=11) 4sec was operated, and it asked for the rate of exhaust air purification in this section.

[0020]

(Example 2)

Except having used the Pt support SrO (2% of Pt support concentration) as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0021]

(Example 3)

Except having used Li2ZrO3 as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.

[0022]

(Example 4)

Except having used aluminum 2O3 as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0023]
(Example 5)
Except having carried out SrO in 150g/piece, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0024]
(Example 6)
Except having used Na2O as CO2 absorber instead of SrO, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0025]
(Example 7)
The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, an evaluation trial (3) and (4) were repeated and it carried out like the example 1 except the line having performed evaluation trial (3) and (S desorption processing) once twice (spacing of S poisoning discharge having been doubled).
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The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made 650 degrees C and NOx catalyst inlet temperature into 600 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber (CO2 having been made not to be emitted from CO2 absorber).
[0027]
(Example 9)
The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made inlet temperature of 720 degrees C and an NOx catalyst into 580 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber.
[0028]
(Example 10)
The same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, about the evaluation approach, temperature at the time of S desorption processing of an evaluation trial (3) was performed like the example 1 except having made inlet temperature of 870 degrees C and an NOx catalyst into 650 degrees C for the inlet temperature of H2 generation catalyst with CO2 absorber.
[0029]
(Example 1 of a comparison)
Except having lost the first catalyst bed, the same actuation as an example 1 was repeated, and the catalyst was acquired. Moreover, the same evaluation approach was performed.
[0030]
[Table 1]

	11モードーHC転化率（％）	(3)の処理1回後のNOx転化率（％）	(3)の処理20回後のNOx転化率（％）
実施例1	82	85	69
実施例2	80	88	75
実施例3	81	87	78
実施例4	81	83	50
実施例5	82	83	60
実施例6	81	85	52
実施例7	82	85	60
実施例8	81	80	55
実施例9	81	80	43
実施例10	82	85	62
比較例1	47	83	67

[0031]
As shown in Table 1, as for the catalyst acquired in the examples 1-10 belonging to the invention in this application, the invert ratio of HC and NOx is compatible. It turns out that especially the catalyst of examples 1-3 is excellent in the NOx invert ratio after durability. On the other hand, the first catalyst bed is not used for the catalyst acquired in the example 1 of a comparison (since there is no zeolite layer, there is no HC adsorption function.). Therefore, the cold HC engine performance gets worse. It accumulates and it turns out that HC invert ratio is low.
Moreover, if an example 1 is compared with examples 4 and 7, when the timing of the case where alkali metal is not contained in CO2 absorber, or S poisoning discharge is behind the graph of drawing 3 , it shows that the endurance of an NOx catalyst falls.

[Translation done.]

* NOTICES *

DRAWINGS

[Drawing 1]

[Drawing 2]

[Drawing 3]

[Drawing 4]

[Translation done.]

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【特許請求の範囲】
【請求項１】
　酸素過剰雰囲気下で運転する内燃機関と、この内燃機関の排気ガス流路に配設するCO_2吸収材、H_2生成触媒及びNOx触媒と、これらCO_2吸収材、H_2生成触媒及びNOx触媒の温度を測定する手段と、排気ガス中の還元成分濃度を間欠的に増大できる還元成分増大手段と、排気ガス温度を高める手段と、を備え、
　上記H_2生成触媒は、水蒸気と一酸化炭素からガスシフト反応により水素を生成し、上記NOx触媒は、該内燃機関から排出される排気ガス中のNOxをリーン時に吸着しリッチ時に還元浄化することを特徴とする排気ガス浄化システム。
【請求項２】
　上記H_2生成触媒を上記NOx触媒より３０℃以上高い温度となるように配設し、上記CO_2吸収材を上記H_2生成触媒と同じ部位又は該H_2生成触媒より上流側に配設して成ることを特徴とする請求項１に記載の排気ガス浄化システム。
【請求項３】
　上記CO_2吸収材を該H_2生成触媒と同じ部位に配設し且つ上流側ほど高濃度とすることを特徴とする請求項１又は２に記載の排気ガス浄化システム。
【請求項４】
　上記内燃機関が自動車用エンジンであって、上記排気ガス温度を高める手段として一定距離走行後にエンジン回転数を高めることを特徴とする請求項１～３のいずれか１つの項に記載の排気ガス浄化システム。
【請求項５】
　上記排気ガス温度を高める手段により昇温された排気ガスが、上記CO_2吸収材からCO_2を放出させ得ることを特徴とする請求項１～４のいずれか１つの項に記載の排気ガス浄化システム。
【請求項６】
　上記排気ガス温度を高める手段により昇温された排気ガスが、CO_2吸収材がCO_2を放出する温度以上且つその温度よりも５０℃高い温度未満であることを特徴とする請求項１～５のいずれか１つの項に記載の排気ガス浄化システム。
【請求項７】
　上記CO_2吸収材の温度を７００℃以上８００℃未満とし、NOx触媒の温度を６００℃以上７５０℃未満とすることを特徴とする請求項１～６のいずれか１つの項に記載の排気ガス浄化システム。
【請求項８】
　上記CO_2吸収材として、７００℃以上でCO_2を放出するものを使用したことを特徴とする請求項１～７のいずれか１つの項に記載の排気ガス浄化システム。
【請求項９】
　上記H_2生成触媒が白金とセリウム酸化物を含み、上記CO_2吸収材がアルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも１種の元素を含む酸化物、炭酸塩又は硝酸塩であることを特徴とする請求項１～８のいずれか１つの項に記載の排気ガス浄化システム。
【請求項１０】
　上記アルカリ酸化物がジルコニウムとの複合酸化物であり、上記アルカリ炭酸塩がジルコニウムとの複合炭酸塩であることを特徴とする請求項９に記載の排気ガス浄化システム。
【請求項１１】
　上記CO_2吸収材が、更に白金を含むことを特徴とする請求項９又は１０に記載の排気ガス浄化システム。
【請求項１２】
　上記CO_2吸収材が、触媒１個あたり２００ｇ以上含まれることを特徴とする請求項１～１１のいずれか１つの項に記載の排気ガス浄化システム

【請求項１３】
　上記ＮＯx触媒が白金及び／又はロジウムと、セリウム酸化物と、アルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも１種の元素を含む酸化物、炭酸塩又は硝酸塩と、を含んで成り、
　３００℃における、該アルカリ金属及び／又はアルカリ土類金属の酸化物とＣＯ₂との反応の生成自由エネルギーΔＧが、Ｈ₂生成触媒に含まれるアルカリ金属及び／又はアルカリ土類金属の酸化物の当該ΔＧより小さいことを特徴とする請求項１～１２のいずれか１つの項に記載の排気ガス浄化システム。
【請求項１４】
　上記ＮＯx触媒に含まれるアルカリ金属及びアルカリ土類金属から成る群より選ばれた少なくとも１種の酸化物、炭酸塩又は硝酸塩と、ＣＯ₂吸収材との量の比が１：４以上であることを特徴とする請求項１３に記載の排気ガス浄化システム。
【請求項１５】
　上記ＮＯx触媒がゼオライトを含むことを特徴とする特徴とする請求項１～１４のいずれか１つの項に記載の排気ガス浄化システム。
【請求項１６】
　上記ＣＯ₂吸収材がリチウムを含み、ＮＯx触媒がバリウムを含むことを特徴とする請求項１～１５のいずれか１つの項に記載の排気ガス浄化システム。
【発明の詳細な説明】
【技術分野】
【０００１】
　本発明は、排気ガス浄化システムに係り、更に詳細には、酸素過剰雰囲気下（リーン雰囲気下）で運転する内燃機関の排気ガスに含まれるＮＯxを低温域（２００～２５０℃）で吸着・浄化し、高温域（６００～６５０℃）でＳ被毒されたＮＯx触媒を再生する排気ガス浄化システムに関する。
【背景技術】
【０００２】
　従来からリーン域のＮＯxを浄化する触媒は種々提案されており、例えば白金（Ｐｔ）とランタン（Ｌａ）を多孔質担体に担持した触媒に代表されるように、リーン域でＮＯxを吸着し、ストイキ～リッチ時にＮＯxを放出させ浄化する触媒が知られている（例えば特許文献１参照）。
【特許文献１】特開平５－１６８８６０号公報
【発明の開示】
【発明が解決しようとする課題】
【０００３】
　これまで、リーンバーンエンジンやディーゼルエンジンでは、ＮＯx吸着触媒を使って、ＮＯxの浄化を行ってきた。かかるＮＯx吸着触媒は、以下のイ～ハ
イ．ＮＯxを吸着する機能
ロ．吸着したＮＯxを脱離する機能
ハ．脱離したＮＯxを浄化する機能
の機能を使用してＮＯxを浄化する。これらの機能のうち、低温域（２５０℃以下）では、ＮＯxの脱離及び浄化が起こらないことがあった。
　一方、このような低温域でＮＯxを十分に脱離、浄化する方法としては、水素の利用が有効である。具体的には、排気ガス中に存在するＣＯを使い、$CO+H_2O \rightarrow H_2+CO_2$という反応を利用して、水素を生成できる。
　しかし、近年では、低燃費化のためエンジンの燃焼効率が上がり、低排温化が進み、排気ガス中にＣＯ₂がより大量に含まれるため、反応が進みにくいという問題点があった。
【０００４】
　本発明は、このような従来技術の有する課題に鑑みてなされたものであり、その目的とするところは、２５０℃以下の低温域でも優れたＮＯx浄化能を有する排気ガス浄化シス

テムを提供することにある。
【課題を解決するための手段】
【０００５】
　本発明者らは、上記課題を解決すべく鋭意検討を重ねた結果、Ｈ₂生成触媒とともにＣ
Ｏ₂吸収材を配設することにより、上記課題が解決できることを見出し、本発明を完成す
るに至った。
【発明の効果】
【０００６】
　本発明によれば、ＣＯ₂吸収材をＨ₂生成触媒に混在させたり近傍に配置することによ
り、低温域でもＨ₂生成反応が進行するようになる。
　また、このＣＯ₂吸収材は一度ＣＯ₂を吸収すると高温にしない限りＣＯ₂を放出しな
い。よって、高温にしてＣＯ₂を放出させるが、このときに排気ガス中の硫黄で被毒され
たＮＯｘ触媒の再生も同時に行える。
　更に、放出されたＣＯ₂をＮＯｘ触媒中のＮＯｘ吸着成分の再炭酸化に使うことで、硫
黄被毒が容易且つより低温で解除される。これにより、耐熱性が向上し、使用貴金属量を
低減できる。
【発明を実施するための最良の形態】
【０００７】
　以下、本発明の排気ガス浄化システムについて詳細に説明する。なお、本明細書におい
て、「％」は特記しない限り質量百分率を示す。
【０００８】
　本発明の排気ガス浄化システムは、酸素過剰雰囲気下で運転する内燃機関と、この内燃
機関の排気ガス流路に配設するＣＯ₂吸収材、Ｈ₂生成触媒及びＮＯｘ触媒と、これらＣ
Ｏ₂吸収材、Ｈ₂生成触媒及びＮＯｘ触媒の温度を測定する手段と、排気ガス中の還元成
分濃度を間欠的に増大できる還元成分増大手段と、排気ガス温度を高める手段と、を備え
て成る。
　このようにＣＯ₂吸収材を配設することで、２５０℃以下の低温域でもＨ₂生成触媒か
らＨ₂がＮＯｘ触媒に供給され、ＮＯｘの脱離・浄化反応が効果的に進行する。また、硫
黄被毒解除の際にＨ₂生成触媒からのＨ₂とＣＯ₂吸収材からのＣＯ₂でＮＯｘ触媒を容
易に再生できる。
【０００９】
　ここで、上記ＮＯｘ触媒は、内燃機関より排出される排気ガス中のＮＯｘを、リーン雰
囲気で吸着し、間欠的にリッチ化することにより吸着ＮＯｘを浄化する。間欠的にリッチ
化するには、例えば、エンジンの運転状態を変えることや、還元成分（Ｈ₂、ＣＯ及びＨ
Ｃなど）を直接供給することなどが考えられる。このため、還元成分増大手段及び排気ガ
ス温度を高める手段を配設して間欠的にリッチ化する。なお、特に、エンジンの運転状態
を変える方法が望ましく、余計な装置を必要とせずにコストを低減できる。
　また、上記ＮＯｘ触媒には、硫黄被毒（Ｓ被毒）を受けるという問題点もある。このＳ
被毒は一時被毒であるため、高温にすれば解除可能であるが、あまり高温に曝すと耐久性
が低下し易い。
　代表的なＮＯｘ触媒であるＢａを例にとれば、Ｓ被毒解除反応はＢａＳＯ₄＋Ｈ₂＋Ｈ
Ｃ→ＢａＣＯ₃＋ＳＯ₂で表される。この式からもわかるように、Ｂａから硫酸が抜け、
炭酸が入ることでＮＯｘ吸収材としての機能が再活性する。ここで、Ｈ₂生成触媒が水素
を生成しつつ、ＣＯ₂を放出すれば、より低い温度でＳ被毒解除反応が進むことになる。
【００１０】
　上記ＮＯｘ触媒としては、例えば、白金、ロジウムのいずれか一方又は双方と、セリウ
ム酸化物と、アルカリ金属又はアルカリ土類金属、及びこれらの任意の組み合わせに係る
ものを含む酸化物、炭酸塩又は硝酸塩と、を含んで成るものを好適に使用できる。
　また、該アルカリ金属やアルカリ土類金属は、２５０℃における、それらの酸化物とＣ
Ｏ₂との反応の生成自由エネルギーΔＧが、Ｈ₂生成触媒に含まれるアルカリ金属やアル

カリ土類金属の酸化物の当該ΔＧより小さいことが好適である。このときは、より低い温度でＣＯ₂を放出し、且つＳ被毒解除も低い温度で行われるため、耐熱性能が向上する。

ここで、生成自由エネルギーΔＧとは、例えば、アルカリ金属をＡとすると、Ａ₂Ｏ＋ＣＯ₂→Ａ₂ＣＯ₃という反応のΔＧを示し、アルカリ土類金属をＢとすると、ＢＯ＋ＣＯ₂→ＢＣＯ₃という反応のΔＧを示す。Ｈ₂生成触媒に係るΔＧを小さくすることで、ＣＯ₂がＮＯｘ触媒の方に吸収され易くなる。この関係が必要なのは、Ｓ被毒解除時、Ｈ₂生成触媒からＣＯ₂を放出する際、できるだけ温度が低い方が良いのと、その温度で放出されたＣＯ₂をＮＯｘ触媒が吸収しＳを放出するためである。

【０００１】

また、上記内燃機関としては、例えば、リーンバーンエンジン及びディーゼルエンジンなどが挙げられる。特に、自動車用エンジンであるときは、上記排気ガス温度を高める手段により、一定距離走行後にエンジン回転数を高めて硫黄被毒解除を行うことができる。この場合は、運転性を損なわず効果的に排温を高められるので有効である。かかる硫黄被毒解除のタイミングは、触媒性能が規制値を超えない時点であれば良く、例えば、ガソリン中の硫黄濃度が５０ｐｐｍである場合、１０００ｋｍに一回程度で足りる。エンジン回転数は昇温制御の入っていない時のエンジン回転数よりも２００～８００ｒｐｍ程度増大させることが望ましい。なお、硫黄被毒解除を頻繁に行うと運転性を損なう恐れがある。

更に、上記内燃機関は、酸素過剰雰囲気下（リーン域）で通常運転されるものであり、この通常運転時の排気ガス温度は２００℃～２５０℃である。この温度域ではＮＯｘの吸着反応は進行するものの、吸着したＮＯｘを脱離して浄化する反応がうまく進まない。

そこで、Ｈ₂生成触媒を配設するのが有効である。上記Ｈ₂生成触媒は、リッチ時の排気ガス中に含まれるＨ₂ＯとＣＯからガスシフト反応によりＨ₂を生成し、吸着ＮＯｘを浄化する還元材として有効なＨ₂をＮＯｘ触媒へ供給し得る。

更にまた、最近の高効率エンジンは排温が低下する傾向にあるため、ＣＯ₂の影響はますます大きい。そこで、本発明ではＣＯ₂吸収材を上記Ｈ₂生成触媒と併用することにより、Ｈ₂生成触媒が十分に水素を生成するのに必要な温度（３００℃以上）が２８０℃程度まで低下する。これより、Ｈ₂生成触媒は２８０℃以上、ＮＯｘ触媒は２００℃～２５０℃になるように配設できる。なお、ＣＯ₂吸収材を使用しないと、排気ガス中に含まれる約１０～１４％ものＣＯ₂により、ガスシフト反応がなかなか進まない。また、排気ガス中のＣＯ₂量が低減するとＨ₂生成量が増大するデータを図３に示す。

【００１２】

上記Ｈ₂生成触媒としては、例えば、白金（Ｐｔ）とセリウム酸化物を含むものが好適である。Ｈ₂生成するためには触媒表面上にＨ₂Ｏの吸着を起こさねばならず、それにはＣｅＯ₂が有効であり、また、ＣＯとの反応にはＰｔが有効である。

また、上記ＣＯ₂吸収材としては、例えば、アルカリ金属又はアルカリ土類金属、及びこれらの任意の組み合わせに係るものを含む酸化物、炭酸塩又は硝酸塩を好適に使用できる。更に、上記アルカリ酸化物（該アルカリ金属やアルカリ土類金属の酸化物）やアルカリ炭酸塩がＺｒとの複合炭酸塩であることが好ましい。Ｚｒはアルカリの安定剤として機能する。

更に、ＣＯ₂吸収材は、更にＰｔを含むことが好ましい。ＰｔはＣＯ₂吸収材に付着したＳを脱離させるので、ＣＯ₂吸収性能を長期にわたって発揮できる。

更にまた、ＣＯ₂吸収材は触媒１個あたり２００ｇ以上含まれることが良い。長期にわたってＣＯ₂を吸収し続けるためには大量のＣＯ₂吸収材が必要となる。

【００１３】

また、上記Ｈ₂生成触媒は、上記ＮＯｘ触媒より３０℃以上高い温度となるように配設できる。このとき、上記ＣＯ₂吸収材はＨ₂生成触媒と同じ部位又は該Ｈ₂生成触媒より上流側に配設することが好ましい。これより、Ｈ₂生成が十分に起こり、それによりＮＯｘ浄化性能も向上する。また、耐久による劣化も抑制できる。例えば、図１及び図２に示すように配設できる。また、上記温度調節は、排気ガス流路の形状を適宜変更することや排気ガスの流速、滞留時間を制御して行っても良い。なお、反応効率を優先し、高温部に

H_2生成触媒やNOx触媒を配置すると触媒の劣化が早く進行し、これを抑制するためには大量の貴金属を使わなければならず、資源面でもコストの面でも望ましくない。

更に、上記CO_2吸収材を該H_2生成触媒と同じ部位に配設するときは、上流側ほど該CO_2吸収材を高濃度とすることが好ましい。これより、H_2生成触媒前段で多くのCO_2を吸収し、下流側のH_2生成触媒のH_2生成能が高まり、NOx浄化性能が向上し易い。

【0014】

上記排気ガス温度を高める手段は、昇温した排気ガスによりCO_2吸収材からCO_2を放出させ得る。即ち、高温の排気ガスによりCO_2吸収材及びH_2生成触媒が加熱され、H_2生成と同時にCO_2が高温ガスとして放出されることにより、S被毒解除温度を低下　　10
できる。

例えば、H_2生成触媒のみではS被毒除去には700℃まで加熱する必要があるが、本発明ではCO_2吸収材を併用するため620～650℃に加熱すれば良い。このとき、昇温した排気ガスは、CO_2吸収材がCO_2を放出する温度以上且つその温度よりも50℃高い温度未満（670～700℃未満）であることが好ましい。排温が高すぎると触媒性能が劣化し易いからである。

また、CO_2吸収材からのCO_2放出やNOx触媒のS脱離を十分に行うためには、上記CO_2吸収材は700℃以上800℃未満とし、NOx触媒は600℃以上750℃未満とすることが好ましい。なお、排気ガス温度が高過ぎると触媒性能を低下させ易い。

更に、上記CO_2吸収材としては、700℃以上でCO_2を放出するものを使用するこ　　20
とが好ましい。例えばLi_2ZrO_3などが挙げられる。

かかる排気ガス温度の制御は、各触媒入口や排気ガス流路上に設けた温度測定手段と、上記排気ガス温度を高める手段を連動させて行うことができる。

【0015】

また、上記NOx触媒に含まれるアルカリ金属又はアルカリ土類金属、及びこれらの任意の組み合わせに係るものを含む酸化物、炭酸塩又は硝酸塩と、上記CO_2吸収材との量の比は、1：4以上であることが好適である。このように、NOx触媒との量的バランスを調整することで、NOx触媒中のアルカリなどがS被毒を受けたときに、それを解除するのに十分なH_2及びCO_2を供給できる。

更に、上記NOx触媒は、ゼオライトを含むことが好ましい。これより、エンジン始動　　30
時等の低温域（室温から150℃）において、HC浄化性能が向上し易い。

更にまた、上記CO_2吸収材としてリチウム（Li）を含有し且つNOx触媒としてバリウム（Ba）を含有することができる。これらLiとBaを混合して使用しても良い。

【実施例】

【0016】

以下、本発明を実施例により更に詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【0017】

（実施例1）

・CO_2吸収材付きH_2生成触媒　　　　　　　　　　　　　　　　　　　　　　　　40

アルミナを酢酸Ce溶液の中に投入し、1時間室温で攪拌した。次いで、120℃で一昼夜乾燥した後、600℃で1時間焼成し粉末aを得た（この粉末aのCe担持濃度はCeO_2として40％）。

粉末aに2％のテトラアンミンPt水酸塩溶液（pH＝10.5）を含浸した。次いで、120℃で一昼夜乾燥した後、400℃で1時間焼成し粉末bを得た（この粉末bのPt担持濃度は2.23％）。

粉末bを427.5g、CO_2吸収材であるSrOを450g、アルミナゾルを22.5g、水900gを磁性ボールミルに投入し、混合粉砕して、触媒スラリを得た。

触媒スラリをコーデェライト質モノリス担体（1.0L、400セル）に付着させ、空気流にてセル内の余剰のスラリを取り除いて130℃で乾燥した後、400℃で1時間焼　　50

成し、コート層４００ｇ／Ｌの触媒を得た（触媒中のＳｒＯ$_2$の量は２００ｇ／個である）。
【００１８】
・ＮＯｘ触媒
　酢酸Ｃｅ水溶液と酢酸Ｂａ水溶液を混合し、攪拌した。次いで、アルミナを投入し、１時間室温で攪拌した。その後、１２０℃で一昼夜乾燥した後、６００℃で１時間焼成し、粉末Ａを得た（粉末ＡのＢａ担持濃度はＢａＯとして７．３％、Ｃｅ担持濃度はＣｅＯ$_2$として２０％）。
　粉末Ａに２％のテトラアンミンＰｔ水酸塩溶液（ｐＨ＝１０．５）を含浸した。次いで、１２０℃で一昼夜乾燥した後、４００℃で１時間焼成し粉末Ｂを得た（粉末ＢのＰｔ担持濃度は１．０４％）。 10
　酢酸Ｚｒ水溶液中にアルミナを投入し、１時間室温で攪拌した。次いで、１２０℃で一昼夜乾燥した後、９００℃で１時間焼成した。更に、６％の硝酸Ｒｈ水溶液を含浸した後、１２０℃で一昼夜乾燥し、４００℃で１時間焼成し粉末Ｃを得た（粉末ＣのＲｈ担持濃度は２．４％、Ｚｒの担持濃度は３％）。
　粉末Ａに２％のテトラアンミンＰｔ水酸塩溶液（ｐＨ＝１０．５）を含浸し、１２０℃で一昼夜乾燥した後、４００℃で１時間焼成し粉末Ｄを得た（粉末ＤのＰｔ担持濃度は３．４１％）。
　酸化セリウムに２％のテトラアンミンＰｔ水酸塩溶液（ｐＨ＝１０．５）を含浸し、１２０℃で一昼夜乾燥した後、４００℃で１時間焼成し粉末Ｅを得た（粉末ＥのＰｔ担持濃度は３．２％）。 20
　ベータゼオライトを６２７．５ｇ、粉末Ｅを９２．６ｇ、シリカゾルを１７９．９ｇ、水９００ｇを磁性ボールミルに投入し、混合粉砕して、第一触媒スラリを得た。また、粉末Ｂを７６７．８ｇ、粉末Ａを５０．５ｇ、酸化Ｃｅを４７．８ｇ、アルミナゾル３３．９ｇ、水９００ｇを磁性ボールミルに投入し、混合粉砕して、第二触媒スラリを得た。更に、粉末Ｃを２７２．０ｇ、粉末Ｄを４０３．９ｇ、粉末Ａを８４．８、酸化Ｃｅを８１．１ｇ、アルミナゾルを５８．１ｇ、水９００ｇを磁性ボールミルに投入し、混合粉砕して、第三触媒スラリを得た。
　第一触媒スラリをコーデェライト質モノリス担体（１．２Ｌ、４００セル）に付着させ、空気流にてセル内の余剰のスラリを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成し、コート層１７２．１ｇ／Ｌの触媒Ａを得た。この触媒Ａに第二触媒スラリを付着させ、空気流にてセル内の余剰のスラリを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成し、コート層１６７．５ｇ／Ｌの触媒Ｂを得た。この触媒Ｂに第三触媒スラリを付着させ、空気流にてセル内の余剰のスラリを取り除いて１３０℃で乾燥した後、４００℃で１時間焼成し、コート層９７．６ｇ／Ｌの触媒Ｃを得た。 30
【００１９】
＜評価方法＞
　以下の試験（１）～（４）を順に行い、（３），（４）の評価は２０回繰り返した。
（１）耐久試験 40
　排気量４５００ｃｃのエンジンの排気系に触媒を装着し、軽油（Ｓ＝１０ｐｐｍ以下）を使用し、ＣＯ$_2$吸収材付きＨ$_2$生成触媒の入口温度を７５０℃、ＮＯｘ触媒入口温度を６５０℃とし、５０時間運転した。
（２）低温活性試験：室温～２００℃
　排気量２５００ｃｃのディーゼルエンジンの排気系に触媒を装着して、１１モードを走り、排気浄化率を求めた。
（３）Ｓ被毒、Ｓ被毒解除処理
　Ｓ濃度５０ｐｐｍの軽油を使用し、ＮＯｘ触媒入口温度を２５０℃とし、１ｈｒ運転を行った後、Ｓ脱離処理（Ｓ＝１０ｐｐｍ以下の軽油を使用し、ＣＯ$_2$吸収材付きＨ$_2$生成触媒の入口温度を７２０℃、ＮＯｘ触媒の入口温度を６５０℃とし、３０分運転）を行っ 50

た。
（４）高温活性試験：２００℃～３００℃
　排気量２５００ｃｃのディーゼルエンジンの排気系に触媒を装着して、リーン（Ａ／Ｆ
＝３０）４０ｓｅｃ→リッチ（Ａ／Ｆ＝１１）４ｓｅｃの運転を行い、この区間における
排気浄化率を求めた。
【００２０】
（実施例２）
　ＳｒＯの代わりにＰｔ担持ＳｒＯ（Ｐｔ担持濃度２％）をＣＯ$_2$吸収材として使用した
以外は、実施例１と同様の操作を繰り返して触媒を得た。また、同様の評価方法を行った
。
【００２１】
（実施例３）
　ＳｒＯの代わりにＬｉ$_2$ＺｒＯ$_3$をＣＯ$_2$吸収材として使用した以外は、実施例１と同
様の操作を繰り返して触媒を得た。また、同様の評価方法を行った。
【００２２】
（実施例４）
　ＳｒＯの代わりにＡｌ$_2$Ｏ$_3$をＣＯ$_2$吸収材として使用した以外は、実施例１と同様の
操作を繰り返して触媒を得た。また、同様の評価方法を行った。
【００２３】
（実施例５）
　ＳｒＯを１５０ｇ／個とした以外は、実施例１と同様の操作を繰り返して触媒を得た。
また、同様の評価方法を行った。
【００２４】
（実施例６）
　ＳｒＯの代わりにＮａ$_2$ＯをＣＯ$_2$吸収材として使用した以外は、実施例１と同様の操
作を繰り返して触媒を得た。また、同様の評価方法を行った。
【００２５】
（実施例７）
　実施例１と同様の操作を繰り返して触媒を得た。また、評価方法については、評価試験
（３）、（４）を繰り返し２回行って、評価試験（３）（Ｓ脱離処理）を１回行った（Ｓ
被毒解除の間隔を２倍にした）以外は、実施例１と同様に行った。
【００２６】
（実施例８）
　実施例１と同様の操作を繰り返して触媒を得た。また、評価方法については、評価試験
（３）のＳ脱離処理時の温度をＣＯ$_2$吸収材付きＨ$_2$生成触媒の入口温度を６５０℃、Ｎ
Ｏｘ触媒入口温度を６００℃とした（ＣＯ$_2$吸収材からＣＯ$_2$が放出されないようにした
）以外は、実施例１と同様に行った。
【００２７】
（実施例９）
　実施例１と同様の操作を繰り返して触媒を得た。また、評価方法については、評価試験
（３）のＳ脱離処理時の温度をＣＯ$_2$吸収材付きＨ$_2$生成触媒の入口温度を７２０℃、Ｎ
Ｏｘ触媒の入口温度を５８０℃とした以外、実施例１と同様に行った。
【００２８】
（実施例１０）
　実施例１と同様の操作を繰り返して触媒を得た。また、評価方法については、評価試験
（３）のＳ脱離処理時の温度をＣＯ$_2$吸収材付きＨ$_2$生成触媒の入口温度を８７０℃、Ｎ
Ｏｘ触媒の入口温度を６５０℃とした以外、実施例１と同様に行った。
【００２９】
（比較例１）
　第一触媒層を無くした以外、実施例１と同様の操作を繰り返して触媒を得た。また、同

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様の評価方法を行った。
【００３０】
【表１】

	11モード－HC転化率（％）	(3)の処理1回後のNOx転化率（％）	(3)の処理20回後のNOx転化率（％）
実施例1	82	85	69
実施例2	80	88	75
実施例3	81	87	78
実施例4	81	83	50
実施例5	82	83	60
実施例6	81	85	52
実施例7	82	85	60
実施例8	81	80	55
実施例9	81	80	43
実施例10	82	85	62
比較例1	47	83	67

【００３１】
　表１に示すように、本願発明に属する実施例１～１０で得られた触媒は、ＨＣ及びＮＯxの転化率が両立されている。特に、実施例１～３の触媒は、耐久後のＮＯx転化率が優れることがわかる。一方、比較例１で得られた触媒は、第一触媒層を用いていない（ゼオライト層がないためＨＣ吸着機能がない。よってコールドＨＣ性能が悪化する。）ため、ＨＣ転化率が低いことがわかる。
　また、図３のグラフより、実施例１と実施例４，７を比較すると、CO_2吸収材にアルカリ金属が含まれない場合やＳ被毒解除のタイミングが遅れている場合は、ＮＯx触媒の耐久性が低下することがわかる。
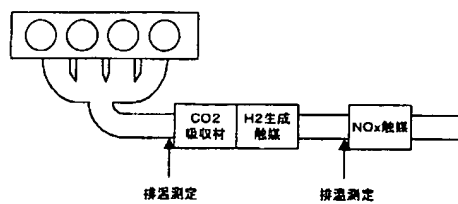【図面の簡単な説明】
【００３２】
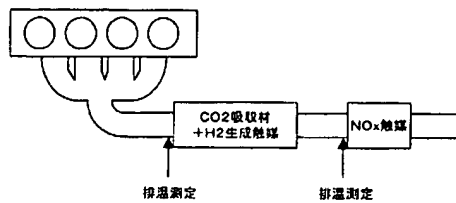【図１】排気ガス浄化システムの一例を示す概略図である。
【図２】排気ガス浄化システムの他の例を示す概略図である。
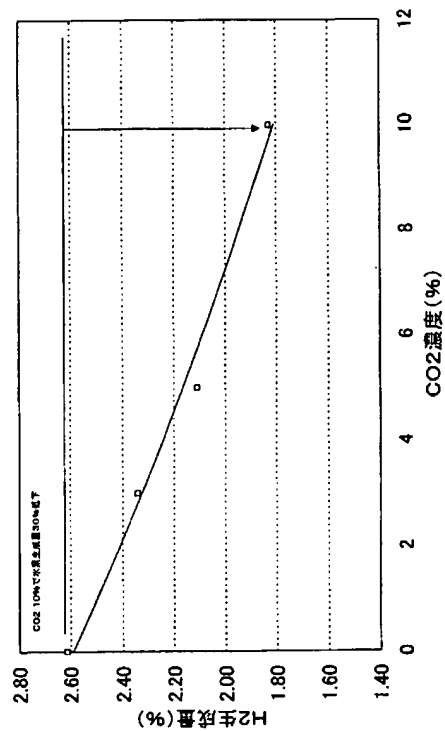【図３】CO_2濃度に対するH_2生成量を示すグラフである。
【図４】Ｓ被毒解除の回数とＮＯx転化率との関係を示すグラフである。

【図1】

【図2】

【図3】

【図4】
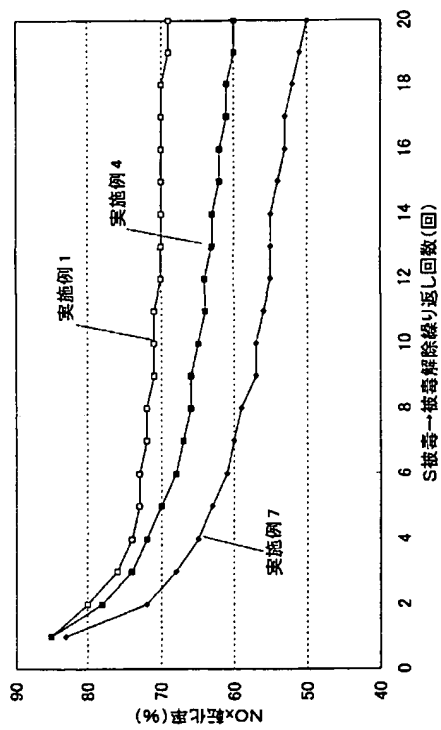
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